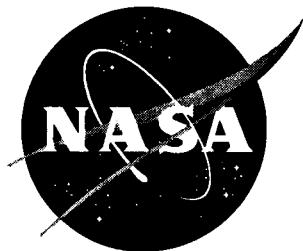


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Characterization of Thin Film Polymers Through Dynamic Mechanical Analysis and Permeation

Helen M. Herring
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June 2003

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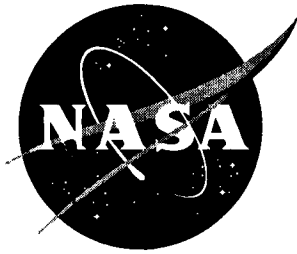
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Characterization of Thin Film Polymers Through Dynamic Mechanical Analysis and Permeation

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Abstract

Thin polymer films are being considered, as candidate materials to augment the permeation resistance of cryogenic hydrogen fuel tanks such as would be required for future reusable launch vehicles. To evaluate performance of candidate films after environmental exposure, an experimental study was performed to measure the thermal/mechanical and permeation performance of six, commercial-grade materials. Dynamic storage modulus, as measured by Dynamic Mechanical Analysis, was found over a range of temperatures. Permeability, as measured by helium gas diffusion, was found at room temperature. Test data was correlated with respect to film type and pre-test exposure to moisture, elevated temperature, and cryogenic temperature. Results indicated that the six films were comparable in performance and their resistance to environmental degradation.

Introduction

Current space transportation systems, such as the space shuttle, use cryogenic tanks for holding liquid nitrogen propellant. These tanks are expendable and are therefore designed to perform only for a single launch. One way to increase the performance of future reusable launch vehicles (RLVs) is to design for reusable cryogenic fuel tanks made from lightweight advanced polymer matrix composite (PMC) materials. One of the chief concerns about reusable PMC tanks is the ability to affect a design that minimizes leakage of nitrogen through the tank walls. The criteria for minimizing leakage are related to both damage tolerance (safety) and durability (life-cycle) issues. The primary failure mode of PMC cryogenic fuel tanks is the development of matrix cracks between plies and subsequent delamination of the laminate.

The PMC cryogenic fuel tank must be able to withstand pressure loads, flight loads, and a wide range of temperatures on both the inside and outside and still retain structural integrity. Combinations of polymers and polymer-based composites have been incorporated into the latest designs including the DC-XA and the X33 demonstration vehicles [1], [2], [3]. These recent PMC tank designs have employed honeycomb sandwich composites and stiffened shell composites for the tank wall structure with varying degrees of success. In both of these programs, laminate design and material selection have been critical to minimizing damage in the PMC. To further enhance leakage control of the cryogenic nitrogen from the composite tank, the addition of thin film polymer sheeting as a liner has been considered. These thin film polymers must display durability and damage tolerance similar to that of the structural tank materials under the same environmental conditions.

Hence, the objective of this report was to experimentally determine what effects environmental pre-conditioning had on the elastic modulus and permeability of selected thin film polymers. Six, commercial-grade, polymer films were selected for testing. These films were pre-conditioned using combinations of elevated temperature, cryogenic temperature, and moisture that were representative of life-cycle conditions. Residual properties were compared to the baseline, as received, condition to evaluate degradation. This report will provide descriptions of the material, test plan, and test methods and compare results as a function of material type and exposure condition.

Materials

The materials in this study, listed in Table 1, were all commercially available thin film polymers employed for numerous industrial applications, including protective surface coatings and food packaging. The Kapton, Metallized Mylar, and Tedlar films all were manufactured by DuPont. Kapton and Mylar are polyimide and polyester films, respectively, while Tedlar is a polyvinyl fluoride. The Eval-F film, produced by Evalca, is an ethylene vinyl alcohol bonded to a polyester substrate. The 3M PUR film is a polyurethane, manufactured by the 3M company. The Paint Replacement film was also manufactured by the 3M company and, like Tedlar, is a fluoro-polymer.

Experimental Procedures

Pre-conditioning

Pre-conditioning was performed to provide data on the influence of temperature and moisture on the residual properties of the films. Large sections from each film were cut for pre-conditioning prior to residual characterization. Baseline samples for each film represented the as-received condition. Including the baseline, four separate pre-conditioning sequences were performed and are given in Table 2.

Aside from the baseline specimens, all samples were placed in an environmental chamber and heated to 50°C with 90% relative humidity for approximately 216 hours. Samples for hygrothermal/cryogenic exposure were subsequently cooled to -184°C for an additional 120 hours. Samples for the cycled exposure condition were hygrothermally exposed and were then thermally cycled from -93°C to 65°C for another 120 hours. After all samples were pre-conditioned, they were removed from the environmental chamber and sealed in plastic sample bags to await residual property testing.

Dynamic Mechanical Analysis

In order to obtain material stiffness as a function of temperature, dynamic mechanical analysis (DMA) was performed on all samples. Briefly, DMA provided a measure of dynamic storage modulus over a range of temperatures. DMA is a standard thermal analysis method, and explanations of the theory and operation for DMA can be found in [4] and [5].

After pre-conditioning, DMA samples were prepared from each of the six materials. At least six separate tests were run for each distinct film and pre-condition. A photograph of the test apparatus is shown in Figure 1. The DMA film samples were cut to be between 5 and 6.5 mm in width and 20 and 30 mm in length to conform to the dimensional limits required for the tension film clamp test fixture. The average thickness for each film sample was based on three separate measurements, taken at the two ends

and the middle of the specimen with a digital micrometer.

The DMA test procedure was as follows: After mounting the film sample in the DMA tension film clamp, the furnace was sealed, and the sample was cooled to -120°C , using a flow of liquid nitrogen. The sample was held at that temperature for 5 minutes. The sample was then heated at $3^{\circ}\text{C}/\text{min.}$ from -120°C to either 100°C or 110°C , depending on the individual material's glass transition temperature, under a preload of 0.5 N. The samples were tested, using a dynamic force with a single frequency oscillation of 1 Hz and amplitude of $20\text{ }\mu\text{m}$. The storage modulus for each run was calculated as a function of increasing temperature, using thermal analysis software included with the DMA apparatus.

Permeability

In order to assess the barrier properties of each film, permeability tests were performed on all samples, using the volumetric gas transmission cell shown in Figure 8. The samples were cut using a 4 in. (10.16 cm.) diameter die punch to conform to the dimensional requirements of the test cell. Film thickness was measured using an electronic thickness gauge. At least three thickness measurements were taken randomly over the sample and averaged.

To test the gas permeability of a film, a sample was placed upon the greased O-ring on the bottom portion of the open test cell. Two sheets of high grade, coarse porosity filter paper were placed atop the film sample, and the top portion of the test cell was lowered onto the base and clamped tightly to seal. A 0.25 mm. radius glass capillary tube was connected to the top of the closed test cell, and a centimeter scale was clamped in position next to the capillary. A compressed canister of helium gas was connected to the test cell at the gas inlet, and constant positive gas pressure was applied to the test cell. All toggle valves were opened to purge any residual air from both the upper and lower portions of the test cell through the oil trap (bubbler).

After purging, all toggle valves were closed, and the helium gas was allowed to saturate the film sample for a sufficient amount of time so as to achieve steady state flow. The toggle valve for the upper outlet vent, located just below the oil trap, was then opened. With a disposable pipette, a single drop of an indicator fluid, consisting of 4-methyl-2-pentanone (methyl isobutyl ketone) and Sudan (III) Red powder dye, was added to the capillary tube and allowed to come to rest at the bottom of the tube. After closing the outlet vent toggle valve, measurements were taken of the displacement of the indicator fluid's top meniscus in the capillary versus time as the helium gas permeated the film. As each measurement was taken, the temperature and barometric pressure were also recorded. Completion of a single run occurred when the top meniscus of the indicator fluid reached the top of the capillary. The outlet vent toggle valve was then opened to return the indicator fluid to the resting position in the capillary, and another permeation run was then started. Two samples from each film were tested for permeability, and three-to-five permeation runs were performed on each film sample to ensure the acquisition of steady state data.

Results and Discussion

Dynamic Mechanical Analysis

Figures 2 through 7 are composite graphs of temperature versus the storage modulus for the different exposure conditions for each film, tested using DMA. Each pre-conditioned film is represented by a single curve, considered typical of its test runs. It was expected that degradation of the film due to pre-

conditioning would appear as a change in the storage modulus data with respect to the baseline condition. Based on the results, changes in the storage modulus as a function of pre-condition for 3M PUR, Eval-F and Paint Replacement were slight as there was little separation in the storage modulus curves for these films. For the Kapton, Mylar, and Tedlar films, however, differences in the storage modulus due to the different pre-conditions were more noticeable.

For every sample, the storage modulus for each individual test run at a given temperature was tabulated, and the average and standard deviation calculated. Table 3 shows the average storage modulus and standard deviation for each film at four specific temperatures in the test run. The scatter in the values was attributed to non-uniform thickness of the film samples and thermal instability of the DMA instrument at very low temperatures. Scatter in the data was also credited to the possible misalignment of the samples in the tension film clamp during mounting. The sudden drop in the storage modulus toward the end of the test for most of the polymers was due to the onset of the glass transition.

Permeability

Permeation data was easily obtainable for the 3M PUR, Kapton, and Tedlar materials. However, there was difficulty in acquiring useful permeation data for the Eval-F, Mylar, and Paint Replacement films. For Eval-F and Paint Replacement, leakage of He gas, due to an inability to achieve an adequate seal in the test cell, caused profuse inaccuracies in the data. Mylar, on the other hand, possessed such good barrier properties that the amount of time required for full saturation of the film and subsequent steady state permeation, exceeded that allotted for these experiments.

Based on the standard method ASTM-D-1434, the capillary displacement versus time data acquired for 3M PUR, Kapton, and Tedlar was used to calculate the permeability of the sample. The method used the following equation to calculate permeability:

$$\bar{P} = \left[\frac{\left(10^{-6} p_0 \times \left(\frac{\text{slope} \times a_c}{ART} \right) \right)}{p - p_0} \right] \times t$$

Where:

$\bar{P}$	=	Permeability
p_0	=	Ambient pressure, Pa
p	=	Upstream pressure, Pa
slope	=	Rate of rise of the indicator fluid in the capillary, mm/s
a_c	=	Cross-sectional area of capillary, mm ²
A	=	Transmitting area of specimen, mm ²
R	=	Universal gas constant, (= 8.3143 × 10 ³ L Pa/(mol K))
T	=	Ambient temperature, K
t	=	Thickness of the specimen

Figure 9 is a composite bar chart, depicting the permeation data for each pre-condition of the three films for which data was easily obtained. It was apparent from the data that the individual pre-conditions had little effect on the permeability of 3M PUR, Kapton, or Tedlar.

Summary and Conclusions

To assess the performance of commercial-grade polymer films as leakage barriers in cryogenic fuel tanks, six distinct thin film polymers were environmentally pre-conditioned and subsequently characterized; using DMA and He gas permeation. Preconditioning consisted of specific combinations of elevated temperature, cryogenic temperature, and moisture for extended periods of time.

Considering material stiffness, it was found that the pre-conditioning of the films prior to DMA testing did not seem to have a significant effect on the measured storage modulus. For the 3M PUR, Eval-F and Paint Replacement films, there was negligible scatter between the test runs, indicating good repeatability. However, scatter in the data increased slightly for the remaining films, Kapton, Metallized Mylar, and Tedlar and was attributed to errors in the test apparatus and material variability. With respect to the environmental pre-conditioning, isothermal (cryogenic) and cyclic temperature (cryogenic to elevated) did not appear to affect the storage modulus of the films. The hygrothermal exposure did affect the storage modulus for Kapton, which is a polyimide. Polyimides are known to absorb moisture, influencing their mechanical properties. Metallized Mylar and Tedlar were not affected by hygrothermal exposure most likely because polyesters and polyvinyl fluoride materials do not readily absorb moisture.

As with the majority of the DMA results, the permeability data of three of the films (3M PUR, Kapton, and Tedlar) showed no evidence that pre-conditioning had any significant effect. Of these three films tested, Tedlar possessed the best barrier properties overall as it showed the lowest rate of He gas permeation when compared to Kapton and 3M PUR. The other three films, Eval-F, Mylar, and Paint Replacement, were not amenable to permeability testing.

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3. NASA, Final Report of the X-33 Liquid Hydrogen Tank Test Investigation Team, George C. Marshall Space Flight Center, Huntsville, 2000, May.
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Table 1. Properties of Polymer Thin Films

Polymer	Average Thickness, mm	T_g¹, °C
3M PUR	0.147	80.7
Eval-F	0.038	99.8
Kapton	0.053	360-410 ²
Metallized Mylar	0.094	70 ³
Paint Rep.	0.099	98.3
Tedlar	0.028	99.1

1. Determined on thin film by Differential Scanning Calorimetry (DSC) at a heating rate of 10 °C/min.
2. Denotes a temperature range at which a second order transition occurs and is assumed to be the glass transition.
3. Temperature for polymer only from DuPont Mylar product literature.

Table 2. Precondition of the Thin Film Polymers Prior to Residual Property Tests

Pre-Condition	Description	Temperature (°C)	Relative Humidity (%)	Exposure time (hours)
1	Baseline	23	Ambient	0
2	Hygrothermal	50	90	216
3	Cryogenic*	-184	Ambient	120
4	Cycled*	-93 to +65	Ambient	120

*Prior to this pre-condition, the material was exposed at 50°C, 90% RH for 216 hours

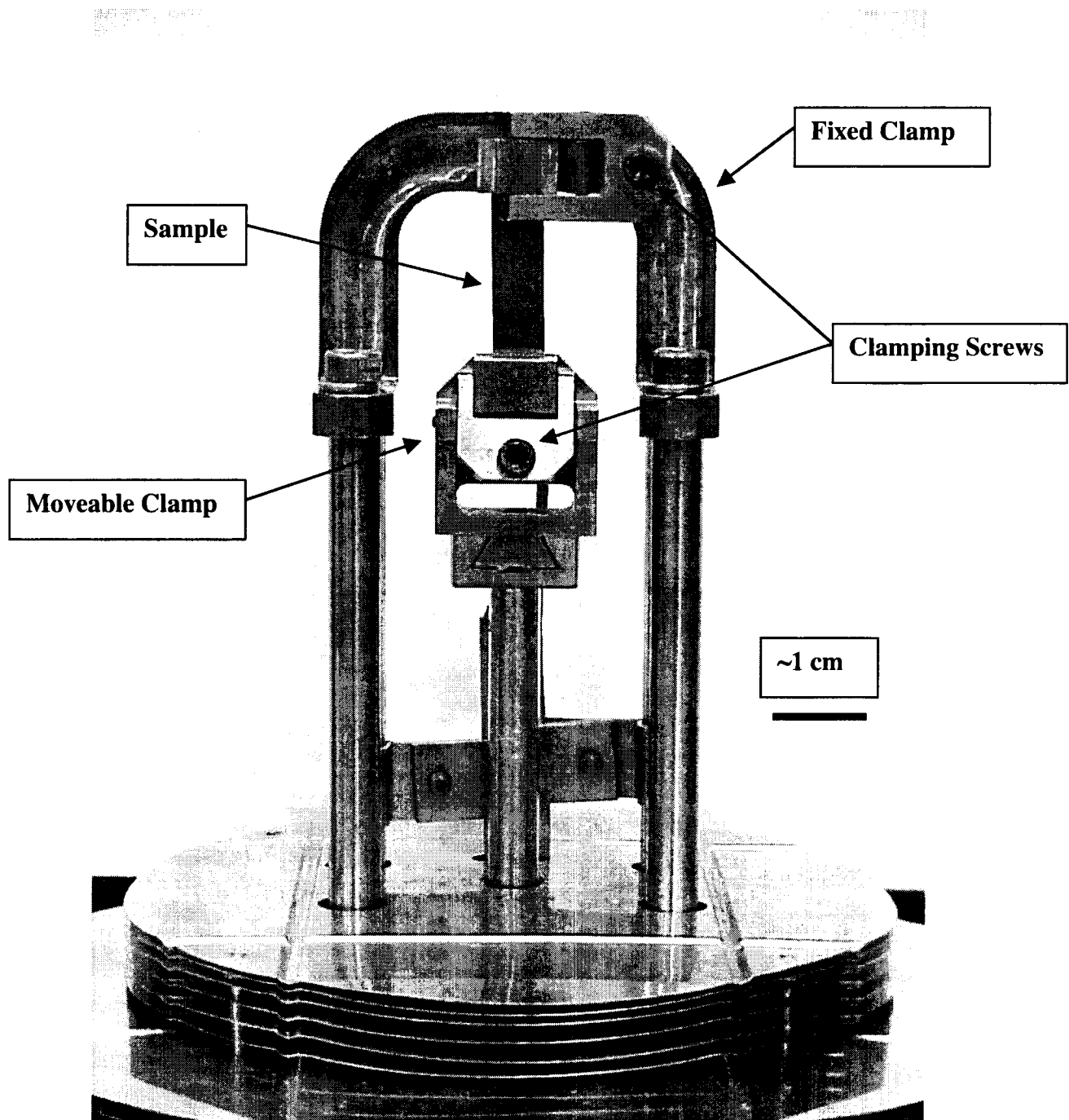


Figure 1. Dynamic Mechanical Analyzer with Tension Film Clamp Installed

Table 3. Average Storage Modulus (MPa) for Four Different Pre-Conditions and Four Selected Test Temperatures.

	-100 °C		-37 °C		26 °C		90 °C	
3M PUR	Avg.	StDev.	Avg.	StDev.	Avg.	StDev.	Avg.	StDev.
1	4077.2	98.1	2666.6	89.6	29.5	5.5	3.5	0.1
2	4238.7	148.4	2763.2	164.7	28.6	3.8	4.5	0.1
3	4412.5	91.7	2844.5	92.4	32.4	2.0	5.6	0.1
4	4201.2	66.8	2685.9	57.9	26.2	2.1	6.9	0.4
Eval-F	Avg.	StDev.	Avg.	StDev.	Avg.	StDev.	Avg.	StDev.
1	2584.2	85.0	1251.7	50.1	330.1	24.9	45.2	3.3
2	2765.4	118.8	1347.9	67.7	330.6	26.0	56.3	1.5
3	2837.1	167.0	958.9	18.6	349.4	15.3	22.4	0.4
4	2471.2	158.0	1243.3	41.0	347.4	23.3	65.5	1.3
Kapton	Avg.	StDev.	Avg.	StDev.	Avg.	StDev.	Avg.	StDev.
1	2683.3	72.1	2231.2	40.7	1915.5	6.7	1651.4	6.0
2	2765.4	118.8	1347.9	67.7	330.6	25.9	56.3	1.5
3	2837.1	167.0	958.9	18.6	349.4	15.3	22.4	0.4
4	2471.2	158.0	1243.3	41.0	347.4	23.3	65.6	1.3
Met. Mylar	Avg.	StDev.	Avg.	StDev.	Avg.	StDev.	Avg.	StDev.
1	3694.1	101.1	2980.1	83.7	1584.2	40.2	1229.9	7.9
2	4110.0	56.2	3192.5	51.3	2062.8	128.9	1451.2	18.5
3	4196.4	79.4	3058.7	52.4	1952.5	80.1	1410.5	23.5
4	3974.0	75.5	2914.3	124.4	1752.0	127.3	1360.5	2.0
Paint Rep.	Avg.	StDev.	Avg.	StDev.	Avg.	StDev.	Avg.	StDev.
1	2911.4	114.2	943.1	29.6	319.2	12.5	8.9	1.1
2	2916.3	56.7	966.7	15.1	354.1	20.9	12.2	3.9
3	2268.6	20.6	1131.2	26.2	281.4	10.5	49.8	1.2
4	2978.5	114.9	986.6	36.1	308.9	6.8	21.2	3.3
Tedlar	Avg.	StDev.	Avg.	StDev.	Avg.	StDev.	Avg.	StDev.
1	4901.5	37.6	2641.5	176.1	1435.3	90.1	250.0	1.8
2	3980.6	746.5	2051.1	57.0	1187.6	29.3	241.1	1.8
3	5024.6	52.1	2810.3	85.6	1581.5	88.7	252.5	2.0
4	5167.5	93.3	2816.1	66.6	1526.0	70.5	293.5	4.5

- 1 Baseline
- 2 Hygrothermally exposed; 50°C, 90% RH for ~216 hours.
- 3 Hygrothermally exposed; 50°C, 90% RH for ~216 hours.
Cryogenically exposed; -184°C for ~120 hours.
- 4 Hygrothermally exposed; 50°C, 90% RH for ~216 hours.
Thermally cycled; -93°C to 65°C for ~120 hours.

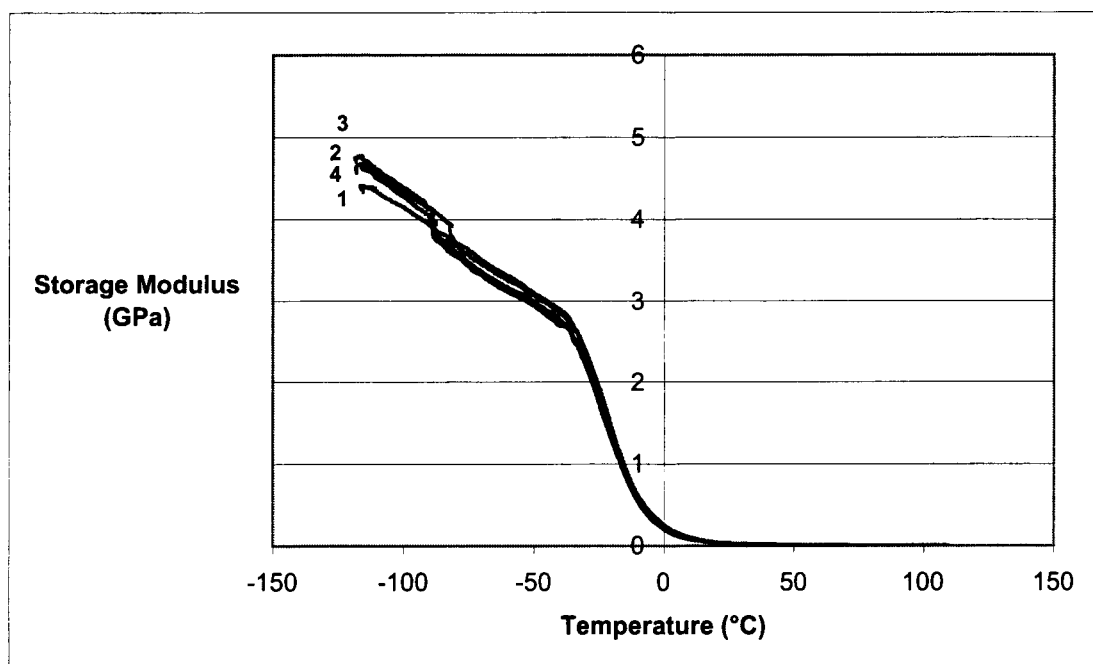


Figure 2. Storage Modulus for 3M Polyurethane Films for Four Different Pre-Conditions as Denoted in Table 2.

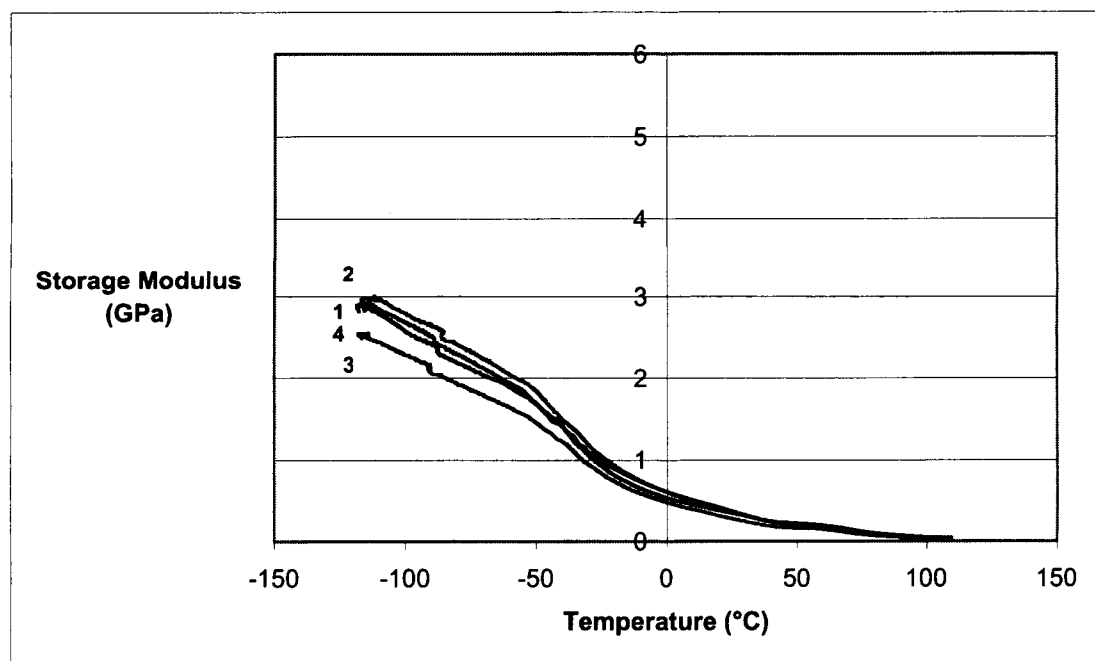


Figure 3. Storage Modulus for Eval-F Film for Four Different Pre-Conditions as Denoted in Table 2.

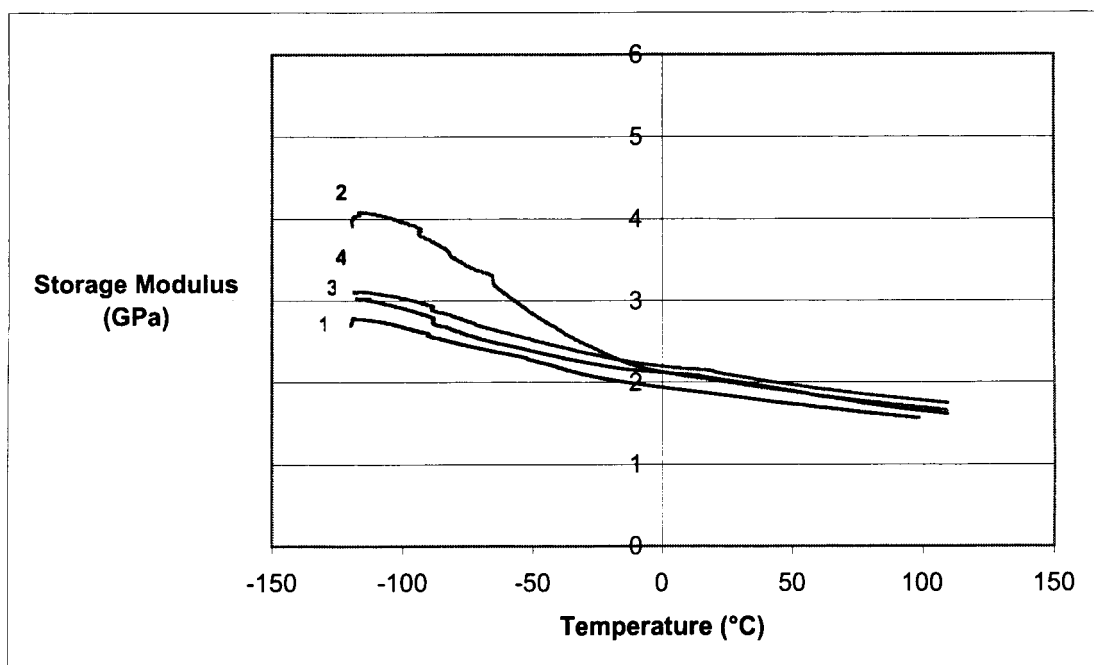


Figure 4. Storage Modulus for Kapton Film for Four Different Pre-Conditions as Denoted in Table 2.

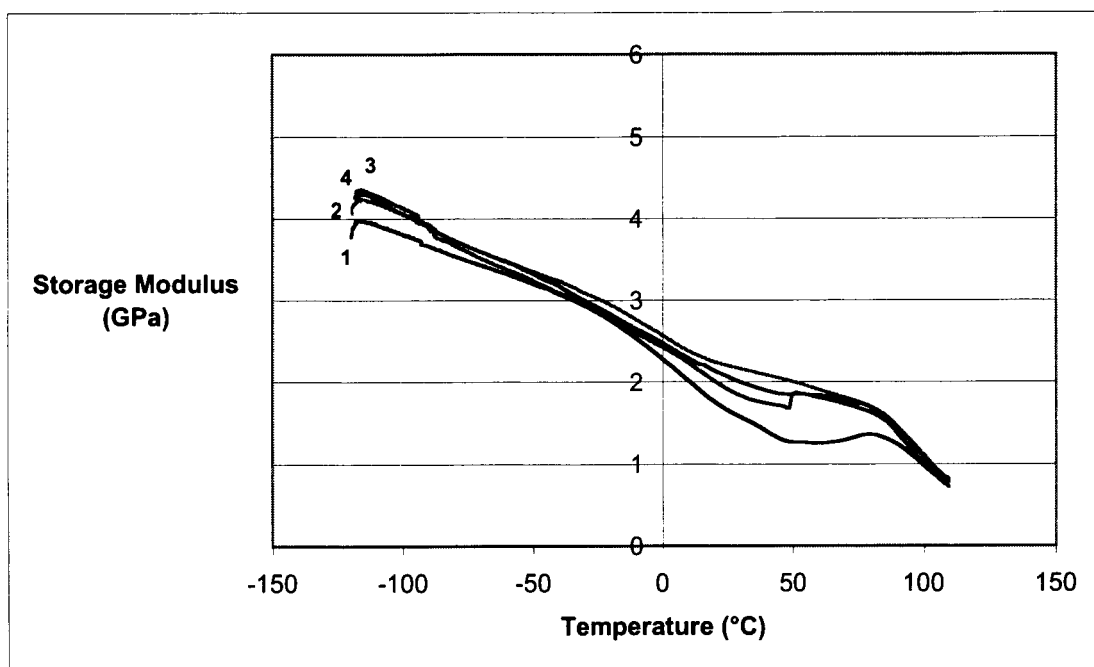


Figure 5. Storage Modulus for Metallized Mylar Film for Four Different Pre-Conditions as Denoted in Table 2.

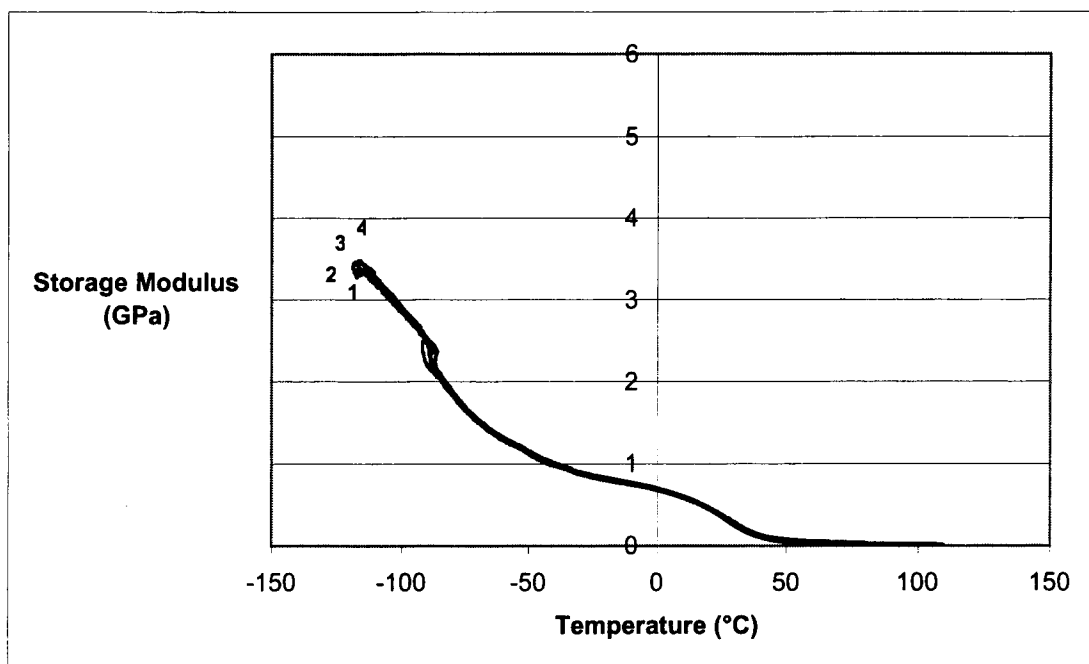


Figure 6. Storage Modulus for Paint Replacement Film for Four Different Pre-Conditions as Denoted in Table 2.

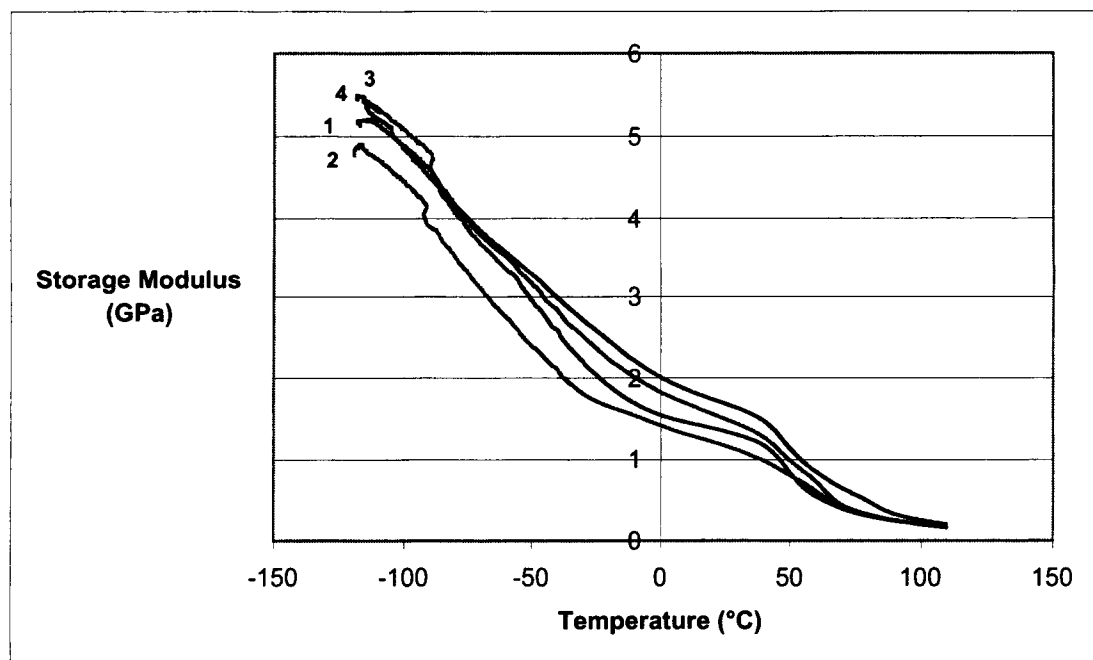


Figure 7. Storage Modulus for Tedlar Film for Four Different Pre-Conditions as Denoted in Table 2.

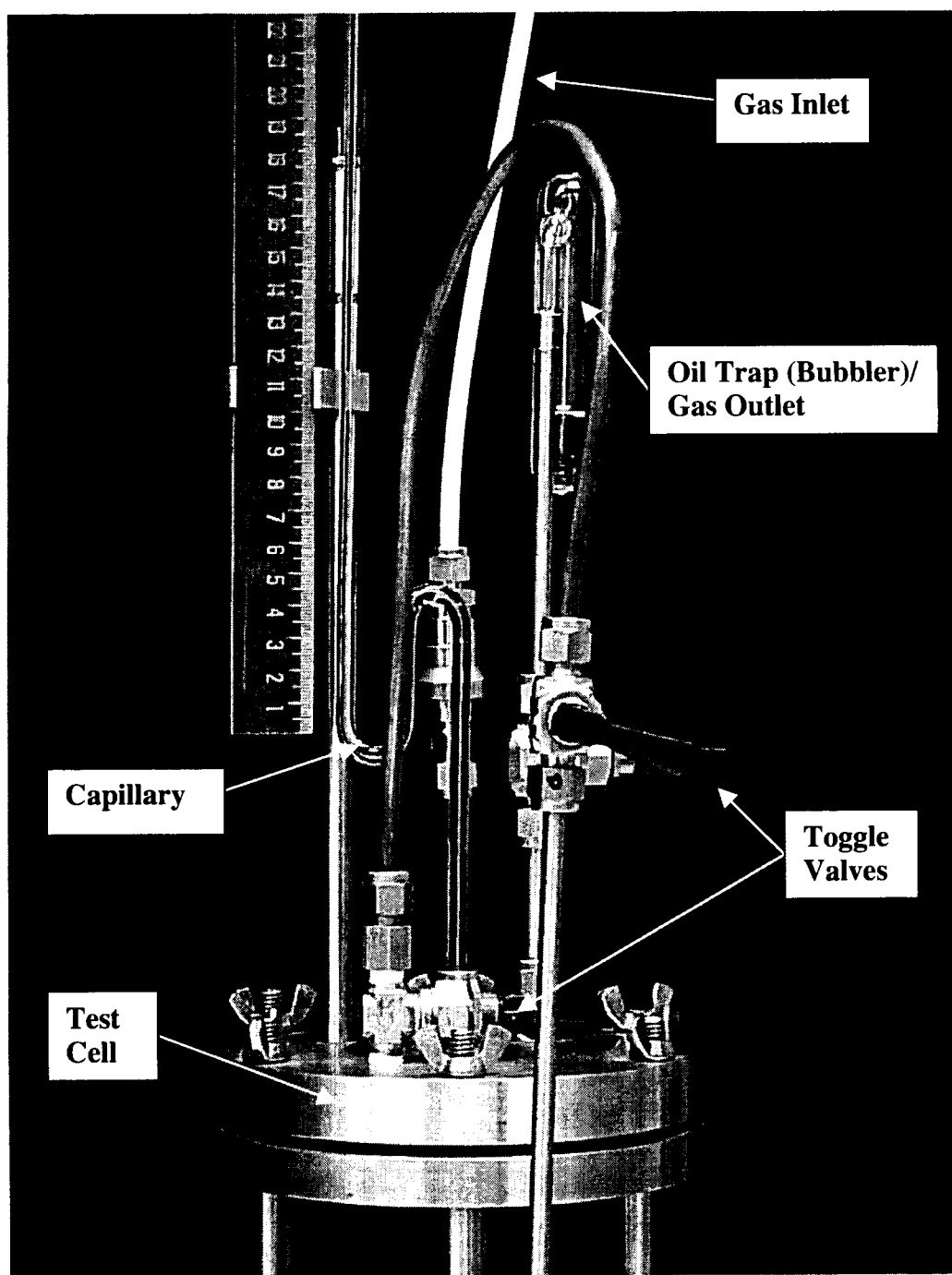


Figure 8. Volumetric Gas Transmission Cell for Permeability Testing of Thin Films.

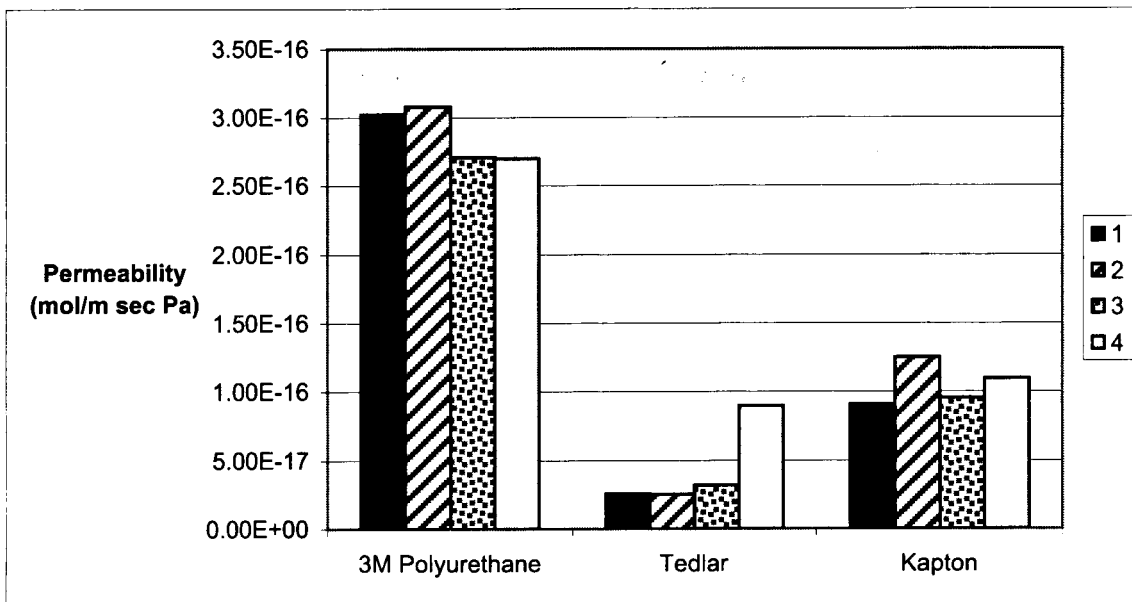


Figure 9. Thin Film Permeability (in mol/m sec Pa) for Three Distinct Polymer Films as a Function of Pre-Conditions 1 – 4 as Denoted in Table 2.

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